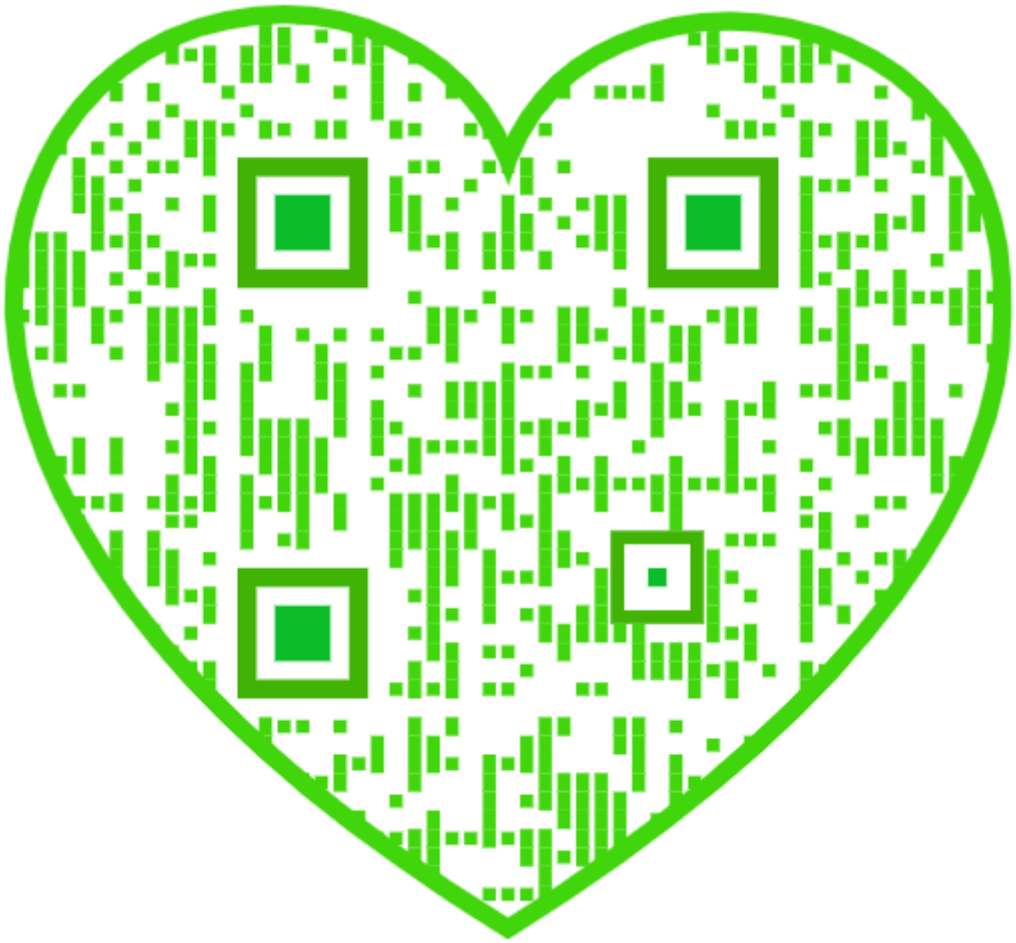
1920
G16

R. P. Gardiner

Examination of Pitch as a possible Source of Resins For Varnish Making



EXAMINATION OF PITCH AS A POSSIBLE SOURCE OF RESINS FOR VARNISH MAKING

BY

ROBERT PARKER GARDINER

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1920

1920
G16

UNIVERSITY OF ILLINOIS

.....191.....

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

.....[illegible]

ENTITLED.....[illegible]

.....[illegible]

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF.....BACHELOR OF SCIENCE in CHEMICAL ENGINEERING

.....

.....J. E. Laymg.....
Instructor in Charge

APPROVED:.....W. A. Noyes.....

HEAD OF DEPARTMENT OF.....Chemistry.....

45[illegible]

ACKNOWLEDGMENT

The author expresses his gratitude to Dr. T. E. Layng; for his generosity in developing the problem at a late and inopportune moment; and for the sincere appreciation that is felt for his encouragement of independent work, and the suggestions which were offered when most needed and which made possible the amount of work done.

TABLE OF CONTENTS

-:-

	page
I - Introduction	1
II - Resume of Previous Work	3
III - Experimental	
a. Foreword	8
b. Preparation of Materials	9
c. Experiments on Pitches	10
d. Experiments on Resinous Content	14
IV - Discussion of Data	17
V - Summary	20
VI - Bibliography	21

THE EXAMINATION OF PITCH

AS A

POSSIBLE SOURCE OF RESINS FOR VARNISH MAKING

-:-

INTRODUCTION

There is rapidly coming to the consumers of coal the realization of a serious problem in the consumption of coal wastefully. Up to the present day, the main sources of waste in that consumption have been three in number: (1), the burning of raw bituminous coal; (2), the coking of coal in bee-hive ovens; (3), the lack of uses for all of the by-products of carbonization. In late years, each of these three sources of waste has been the object of considerable research work, the results of which have caused the world consumers to realize the value of using coke, and utilizing the by-products for other than their heating value. The latter especially, has come to be a very important matter, and up to the present time, all of the by-products of the coking process are utilized in important ways, except the tar. In the investigations carried on with the latter, it has been cut at three different temperatures, 240, 300, and 360 degrees C, giving soft, medium and hard pitches. The oils produced, have found great use for creosoting and in the coal tar dye industry. But the pitch produced has become a drug on the market, being used to only a limited extent for road-making, roofing felt, in roperies, etc; none of which take up the whole supply. Research has shown that there is a consider-

able quantity of resins present in coal tar pitch, and the fact has been the basis of investigation of the possible use of the pitch in the manufacture of a varnish.

There is at present, a great demand for a varnish that can be used as a covering for iron, stone, and wood work that is subjected to the attack of acids, gases, or water. Such a varnish must be produced at a low price, because of the nature of its use. This is a difficult problem in view of the high present day prices or resins suitable for such a varnish. Investigation has shown that the resins present in the coal tar pitch are entirely satisfactory for such uses, and that the varnishes so produced are even better protectors than those made from the other types of resins. However, such varnishes produced up to now, are of very crude quality; they are black, thick, and very difficult of application, besides requiring a more or less complicated method of manufacture.

RESUME OF PREVIOUS WORK

The examination of pitch as a possible source of resin for the manufacture, is a subject of but recent investigation, and in regard to low temperature pitch, there is no record available prior to 1917. However, there has been considerable work done on tar, and upon pitch other than that from low temperature tar. The work is described mainly in patent literature and is undoubtedly incomplete in its details. The first report available on tar or pitch, is that of Chaumont, published in 1865.* By using a solution of bitumen, asphalt or resin in carbon bisulfide, he was able to produce a finish which he used as a covering for wood, stone, or iron work. The amounts he used are: 100 parts of bitumen, with 80 - 100 parts of CS_2. Or, if asphalt is used; 300 parts of asphalt to 100 parts CS_2. The asphalt or bitumen is poured into a tub, the CS_2 is added, closing the tub to prevent the loss of CS_2. The mixture is heated for from 12 - 24 hours at a medium temperature, when the liquid is drawn off. The liquid is usuable as a varnish for the above purposes. However, the odor is so objectionable that the process is not used to any great extent.

Between 1865 and 1909, the use of tar and pitch was greatly developed in England and Germany, for manufacturing roofing felt, in roperies etc. As a corollary to these uses, the pitch was utilized in the production of a varnish, for iron work especially, but also for wood and stone work. These var-

---

* Wagner's Jahresbericht 1865 p 686

nishes were made in a very simple way, by melting the pitch with the various products of tar distillation, and did not require the addition of any foreign matter. No plant was necessary except an open pan set in a covered place, heatable from without. However, it was preferable to use a closed pan, with a mechanical agitator if possible. A melting pan of wrought iron was found to be best, as it prevented the occurence of any cracking, which is very dangerous in this case.

In this pan the whole quantity of pitch is melted and worked up with a little of the oil to be used, being sure to let the pitch cool down before the oils are added, to prevent their loss by evaporation. However, the cooling must not go so far as to allow the mass to solidify. Then the remaining oil is added gradually, and with stirring. The addition is continued until a sample taken out possesses the right consistency.

The commonest kind of varnish is made in the manner just described, from creosote oil and pitch. But even a simpler method of operation may be employed when they are used. The tar is distilled until the middle portion has passed over, approximately 240 degrees C, when the fire is drawn out. The pitch is allowed to cool a little, and the residue is diluted in the still itself, with oil to the amount of 3/4 of the weight of the pitch; the resulting liquid is used as a varnish. Or else the tar is distilled to hard pitch(in order to obtain the anthracene) and the oil (freed from anthracene and naphthalene) is run in to the proper degree of thinness, stirring during the addition. Tar that is prepared in this way is known in Germany and in England as"prepared tar", or "artificial Stockholm tar".

It penetrates very quickly and very deeply into the wood and is greatly recommended as a painting for wood or other work that is subject to the action of acids, chlorine, etc. It is very thick in body and as a result, is only applicable to the roughest iron or wood work. However, for such purposes, it is excellent.

A better varnish than this is obtained by following a method as the above, but, instead of the light oil distilled from the tar, using the last fraction from the light-oil still, or the oil taken from the carbolate of soda, as described by Lunge*. For 100 parts of moderately hard pitch, about 60 parts of the light oil is used. This varnish leaves a more lustrous and smooth coat than the above, and also gives a thinner and more easily applied liquid, so that it can be used for finer iron work.

More quickly drying and thinner varnishes have been made in all gradations by substituting naphtha for a part of the light oil. The pitch is first worked up with all of the light oil, and then the naphtha is added, being sure that the temperature of the mixture is low enough to prevent the volatilization of the naphtha. Also, very long and continuous stirring is necessary, since the naphtha is not so easily incorporated with varnish as the heavier oils, and the varnish would separate into a black deposit with the naphtha floating on top of it. By this means, a varnish may be prepared which will dry in an hour, and which is very good for hardware, where the color is of no consequence. Instead of the coal tar naphtha, petroleum

---

* Lunge "Coal Tar and Ammonia vol. II P 567

spirit may be used.

Because of the commercial nature of the problem, most of the literature available on this subject appears in patent notices. A patent of Marchisis and Stevens* (Sept. 23, 1879) seeks to improve the above varnish by heating it with bleaching powder or with a solution of common salt, and washing with copperas solution. The success of this attempt is not known.

Watson Smith (private communication)** recommends as a good varnish for tarpaulins, one obtained by melting wood-tar pitch with the same weight of coal tar creosote oil; also as a good metal varnish, one obtained by melting 6 lb. of dark rosin with a pint of linseed oil and a gallon of creosote oil, to be mixed, for finer work, with a little gum and any kind of coloring matter.

E. Heusser (German Patent #24231)*** makes a black paint by extracting pitch from coal tar with warm light tar oil, or with benzoline. The residue that is left is used in making the paint.

Roth (German Patent #152,758)**** produces a compound which he used for protecting iron and cement work under water, by using 33 parts of heavy oil, and 47 parts of pitch and aluminium oleate. The product was sold under the name of "Inertol"

---

* Lunge " Coal Tar and Ammonia" Ed. 4, p 445
** " " " " " Ed. 4 p 446
*** " " " " " Ed. 4 p 446
**** " " " " " Ed. 4 p 446

In 1911, O. Sprenger (German Patent # 254,767)* purified coal tar distillate between 180 - 250 degrees C with soda lye and sulfuric acid. Then, using 100 parts of the purified oil, he added 5 - 10 parts of an animal or vegetable oil (tallow or linseed), and then 2% by weight of concentrated sulfuric acid with stirring, keeping the temperature below 50 degrees C. He then stirred for one hour at that temperature, during which time SO_2 was evolved, allowed the mixture to settle, removed the resin acid from the bottom, added freshly slacked sludge, stirred, and oxidized the mass with ozone or with air containing ozone. The SO_2 was oxidized, and the lime combined with all of the sulfuric acid, and settled to the bottom. The excess $Ca(OH)_2$ saponified all of the acid contained in the oil. The tar oil varnish is drawn off from the sediment as a clear brownish yellow oil. Mixed with color, it forms an excellent coating for iron stone and wood work.

In 1916, R. MacLauren took out British patent #108448** By using low temperature tars, consisting of paraffinoid hydrocarbons, he obtained a resinous substance by separating it from the oily portion of the pitch with a hydrocarbon oil such as paraffin oil or gas oil, in which the resinous portion is insoluble. He added water to help in the separation, shook and allowed the resins to settle. The oil was separated from the water and used as a lubricant. The resins were purified by using a light petroleum oil, after which it was dissolved in benzene, methylated spirits etc, and used as a varnish.

---

* Chem. Abstracts 1911 p
** " " 1917 p 3116

EXPERIMENTAL

In this investigation, the object has been to find a method for utilizing the resins in pitch for manufacturing a varnish suitable for iron, wood, and stone work. The work has been carried on by the two general methods of proceedure: (1), attempting to produce a varnish using the three different kind of pitches, and (2), trying to increase the resinous content of the pitch. The experiments have been made with the idea of producing a varnish of better color and body than has been done thus far, by a more simple and inexpensive method of manufacture.

The pitch used in the investigation, was produced from tar obtained from O. Holzman. The tar was the by-product of his investigation of the low temperature coking of coal as developed by Prof. S . W. Parr and Dr. T. E. Layng.

Preparation of the pitch:

Each of the three types of pitch were produced, using straight distillation and cutting at the correct temperature. The distillation was carried on by using an electric furnace, large enough for a two litre flask, heated by number 16 chromel wire. Its heating had a maximum of 600 degrees centigrade, which was attainable only after three hours of maximum current, and the temperature was regulated by means of a carbon plate rheostat. An asbestos hood for covering the neck of the flask, simplified the distillation of the tar containing water.

In the first run, the two litre flask was half filled with the mixture of tar and water obtained from O. Holzman, and was placed in the electric furnace, then connected to a common Liebig condenser. The temperature of the furnace was regulated so as to be not more than 50 degrees higher than the temperature of the distillate coming over. Four hours were required for a quantitative determination of the water. The tar, then dry, was distilled, cut at 300°C, and the pitch was used for experiments for producing a varnish. The oils produced were turned over to R. M. Pearson to be used in his work on the hydrogenation of oils.

The same proceedure was followed in the second run, except that a portion of the pitch cut up to 340°C was taken out, as was done at 300°C, and at 340°C, giving samples of the three types of pitch necessary for the experiments.

Preparation of the linseed oil:

The vehicle used, was boiled linseed oil. It was produced by heating raw linseed oil in an open enamel dish over a circular burner for three hours at a temperature of 240°C. The result of this heating was a light colored oil which dried quickly, and which is termed boiled linseed oil.

Preparation of a drier:

When the advisability of using a substance which would cause the varnish to dry more quickly, was considered, it was found that the most satisfaction would be obtained with Manganese borate. About 150 grams were made by adding a 10% solution of $MnSO_4$ in water, to a sodium borate solution, heating, filtering, and drying the precipitate at 100°C.

Experiments on producing a varnish with pitch:

The first run was made using pitch cut at 300°C. 34 grams were ground fine, and heated to melting in an open enamel dish over a circular burner. 50 grams of boiled linseed oil were then added, and the mixture was stirred. But it congealed, and would not mix at all, which seemed to be due to the cold oil added. So the run was repeated, adding hot linseed oil. The mixing took place with greater ease; it was stirred occasionally, and was heated for one half hour. It was then allowed to cool, and benzene was added as a thinner, until the mixture was thin enough to prevent hardening when cold. After cooling, it was thinned to the proper consistency and tested by applying to a glass surface,

(watch glass), and leaving to dry. The drying required four days, and the coating was too gummy and yellow, indicating an excess of linseed oil. Moreover, there was remaining in the heating pan, a large piece of what seemed to be carbonized pitch, weighing about 30 grams. This indicated an incomplete mixing of the oil and the pitch. The whole run was repeated using as a thinner, turpentine instead of benzene. The only improvement was that the varnish dried in three days instead of four.

A test was made on the residue above, to determine the degree of carbonization. A Soxhlet extractor with an asbestos thimble was used, and phenol was used as the solvent. After five hours of extraction, the absence of residue in the thimble showed the residue above to be of hydrocarbons; and hence that the less residue in a run of varnish, the more resin would be mixed with the oil to give a better varnish.

The second run of varnish was made using the same amounts of constituents and the same apparatus. The mixture was heated for 1 1/2 hours with more constant stirring, taking care in the melting of the pitch to see that the temperature was not so high as to cause the pitch to volatilize. The mixture produced was allowed to stand a longer time before testing; and when finally tested on the glass, it dried in two days, gave a sturdier coating, and a more brown color, indicating a more thorough mixing and heating. The residue in this case was found to be only 14 grams.

Following the information obtained in the first 3 runs, the same proceedure was emoloyed, heating for three hours, with almost continuous stirring. The tests showed the mixture

would dry in about 1 1/2 days, the color was better, and the coating was noticeably harder. The residue in this case was 9grams.

The above results are summarized in the following table:

Run	Heat and att'n	Residue	Varnish
(1)	1/2 hr. with little stirring	20 gms.	Yellow, gummy and no body
(2)	1 1/2 hrs. with more stirring	14 gms.	Browner and better body
(3)	3 hrs. with continuous stirring	9 gms.	Rich brown and harder coating

These experiments showed the necessity of keeping the temperature low, adding hot linseed oil, stirrinf constantly, and heating for at least three hours.

Because the varnishes so produced were more or less soft, it was decided to experiment on the different cuts of pitch. For this work the pitch cut at 240°, 300°, and 340°C were used. The same apparatus and the same method as above were used, and the following results were obtained;

Cut	Wt. pitch	Wt. residue	Varnish
240 C	34 gms.	6.5 gms.	Good color, but gritty and not very hard.
300 C	25 gms.	6.0 gms.	Good color, a little harder, good body
340 C	30 gms.	7.0 gms.	Good color, good body, harder, but required 2 days for drying.

These experiments point out the advantageous use of hard pitch cut at 340°C, so further experiments were made in an

endeavor to produce a satisfactory varnish with it. In all of the above work, one of the chief faults was the softness of the coating, which seemed to be due to an excess of linseed oil. The following table shows the results obtained by using various percentages of linseed oil, following the same method of preparation as above;

Weight of pitch	Weight of linseed oil	Weight of residue	Kind of varnish
25 gms.	20 gms.	10 gms.	gritty, hard to thin, and difficult to apply. Heavy coat that was rather hard.
25 gms.	25 gms.	8 gms.	not so gritty, but otherwise the same as the above
25 gms.	37 gms.	6 gms.	much better body, good color, easily applied, and best as to hardness. It dried in 1 1/2 days.
25 gms.	50 gms.	6 gms.	color good, but the coating was softer than the above.

The above table shows readily that the best proportion of the oil to the pitch, is 60 - 40, by weight, and further tests were made on it. Because of the length of time required for drying, it was decided to determine what effect the presence of a drier would have on the varnish produced. The proportions used were: 25 grams of pitch, melted and about 5 grams of Manganese borate added, then the 37 grams of linseed oil finished the mixture. The varnish so produced, did dry in about a day, but its color was changed from a tan to a dark brown; the hardness

evidently was not effected in the least.

Further tests were made on the last varnish, with and without the drier, for hardness, (scratching the coat with a knife), for body by running on a piece of glass, this also for color and clearness; a sample of each of the varnishes was left to stand one week in contact with water, HNO_3, and HCl. The following is a table showing the results of these tests:

Test	Without drier	2% drier
Water	no effect	no effect
HCl	" "	" "
HNO_3	discolored, but did not eat it	discolored, but did not eat it
Hardness	tough, but not hard brittly	a little more brittle than the other
Color	good varnish color	a dark brown
Body	had good covering power	also had good covering power.

Experiments on increasing the resinous content of pitch.

It is a known fact that nitration increases the amount of resins in coal, and following the work on the pitches, experiments were performed to use this fact in the production of a varnish. The coal used was Pocohantus, ground in 1908 and sealed in a glass jar. 25 grams were heated with 100 cc of 20% HNO_3 over a steam bath, to dryness. A Soxhlet extractor with an asbestos thimble was used to obtain the resins, using phenol as the solvent. But the asbestos thimble could not hold any appreciable amount of the coal without breaking; moreover the phenol would not reach the caked interior, and after 24 hours heating, no dissolution

taking place, a different method was tried. The coal was heated in a beaker with the phenol; the solution was then run into the thimble by means of a separatory funnel. The extraction was very slow, requiring over 24 hours for completion. An alundum thimble was then tried, but it did not improve the time very much. When the extraction was finally completed, the phenol solution was distilled, but instead of producing phenol and a resinous residue, after the phenol was off, there was left only a coke.

The same procedure was gone through, using more acid and heating more quickly; also using just the coal in the extraction. The same results were obtained in each case, and the work was abandoned.

Next were taken up the experiments on the oils contained in the pitch. All pitch remaining was distilled in a cast iron still using the electric furnace. No provision was made to keep the arm warm, and when the apparatus was left for a time, the oils congealed in the cool arm and clogged it up. As a result, all of the oil escaped through the cracks, and the run was ruined. The attempt was repeated using what pitch could be found, keeping the arm warm. It was successful, and the oil obtained was subjected to a current of air in a filter flask over night. The oil was effected materially, being more firm and sticky. It was used in the place of pitch to produce a varnish as was done with the pitch. When tested, it was found to dry quickly, but left a very soft coating of good color. It was not very satisfactory.

During the first part of the work, a varnish was produced by following M Chaurons patent. In lieu of gas oil, ker-

osene was employed. To the tar was added the kerosene, and a quantity of water. After shaking, the resins were separated from the oils by means of the water, and were removed very easily. They were mixed with benzene as a thinner. The varnish resulting was black in color, and rather difficult to apply because of its viscosity.

DISCUSSION OF DATA

The greater amount of data was secured from the experiments on the various pitches,- which determined to a large degree, the utility of pitch as a resin for varnish,- and wherein the resin in the best form is to be found.

In producing the varnish, the first determination made, was the proper time of heating; the results of heating for 1/2, 1 1/2, and 3 hours proving that the longer period was the best for a more complete mixing of the pitch and the oil. Using this fact, experiments were performed to find the best cut of the pitch. Here the results showed that the lower cuts did not necessarily contain the resins, but that the hard pitch contained them in the best condition, for the varnishes produced from the lower cuts were not hard- possibly due to the presence of anthracene &. The cut which excluded the anthracene gave the hardest varnish; this was the pitch cut at 340° C.

It was found however that the varnish produced was not nearly hard enough, and seemed to possess too great proportion of linseed oil. Thereupon, various proportions of oil and pitch were tried, and resulted in the finding that a proportion of 60 parts oil to 40 parts of pitch gave a varnish harder than the others and of just as good color. This varnish proved to be very satisfactory,- drying in less than 1 1/2 days, and possessing good covering power, besides being very resistant to the action of acids and of water.

The best method of production used, was to heat for over three hours in an open dish at a temperature low enough

to prevent volatilization of the pitch; and stirring constantly. Then to allow the mixture to stand after adding turpentine, before applying. The varnish produced in this way compared very favorably with the varnish prepared by following MacLauren's patent. Its color was much better; it was more easily prepared; it dried in half the time; but it was not so hard.

The same varnish was compared with the varnish produced from the oils obtained from the pitch up to coke. The latter varnish was very soft, and did not possess very good drying qualities. This comparison shows that the pitch as such contains the best resins for a varnish. The effect of a drier on this varnish is to cause a quicker drying, but it also causes the varnish to become darker in color.

There are several objections to the production of a varnish in the above manner. The first is in the use of linseed oil, because of its high price. Experiments were not tried using China wood oil, but such a method should produce a varnish of as good properties, and much cheaper in its cost of production. A further difficulty was found in the attempts to produce a real hard varnish. Those produced were rather hard, but not as varnish is usually classified.This leads to the suggestion that it might be possible to produce a varnish using a mixture of colophony and pitch as the resin, or using some other hard rosin. The last objection is the fact that a residue is left in each run, which is not carbon,- it is a hydrocarbon, and should be usuable in the varnish. An investigation as to its character might result in a knowledge of how to conduct a more thorough mixing, and hence how to produce a better varnish.

In these experiments, a distinct advantage in obtaining favorable results was the use of low temperature pitch. To be successful in producing a varnish, a pitch of the highest resinous content possible, with the lowest possible percent of free carbon, should be used. The extraction test using phenol, showed that there was no free carbon in the low temperature pitch, and the fact that it was entirely soluble in the phenol showed that it must have contained a large percentage of resins. With high temperature pitch, such conditions would be impossible, for that pitch contains as high as 40% free carbon. This would make the mixing of the oil and the pitch difficult, and the varnish produced would not be hard nor durable, because of the low proportion of resins as compared with the oil.

SUMMARY

I - The most successful runs were made by using hard pitch; pitch cut at 340 C.

II - The best quality varnish was produced using the proportion of 60 parts of oil to 40 parts of the pitch.

III - The method found to be the best was: to heat in an open pan, keeping the temperature down to prevent the volatilization of the pitch, stirring constantly, and allowing the mixture to stand for some time after adding the thinner.

IV - The varnish produced was of better color, body and covering power, than the varnish produced by following existing patent methods. However, it was not so hard.

V - The resins as they existed in the pitch, were better for varnish making than the oils distilled from the pitch even after oxidizing them with a stream of air,

VI - The nitrating of the coal as a method for increasing the resinous content, was abandoned because of the difficulties met in the experiments.

VII - The varnish produced, underwent the water and acid resisting tests in very creditable manner, showing that it is possible to produce a varnish from pitch which would be very satisfactory as a covering for iron, stone, or wood work that is subjected to the attack of either acids or of water.

BIBLIOGRAPHY

(1) Wagner's Jahresbericht 1868 page 886

(2) Lunge's Coal Tar and Ammonia vol. I-page 441 - 446

(3) Lunge's Coal Tar and Ammonia vol. II- page 567

(4) Chem Abstracts 1911 page

(5) Chem. Abstracts 1917 page 2116